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(54) Title: COATED NANOFIBER WEBS

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(57) **Abstract:** The present invention is directed to a method of forming nonwoven webs comprising coated fibers. The method of forming the nonwoven web generally comprises the steps of forming fibers from a melt fibrillation process, forming at least one fluid stream containing a coating substance, applying the coating substance onto the surface of the fiber, and depositing the coated fibers on a surface to form a web. Typically, the fibers are coated in flight. Preferably, the melt fibrillation process to form the fibers is a melt film fibrillation process. A melt film fibrillation process generally includes the steps of providing a polymeric melt, utilizing a central fluid stream to form an elongated hollow polymeric film tube, and using air to form multiple nanofibers from the hollow tube. The nonwoven web may comprise a layer having a significant number of nanofibers with diameters less than one micron. The layer may comprise two or more pluralities of fiber diameter distributions wherein at least one plurality has an average fiber diameter of less than about one micron. The coating substance can be selected from the group consisting of lotions, powders, surfactants, softeners, nanoparticles, creams, gels, conducting fluids, hydrophilic agents, hydrophobic agents, hygroscopic agents, emollients, plasticizers, absorbent gelling material, antimicrobial agents, and combinations thereof. A preferred coating substance is a surfactant. Another preferred coating substance is a hydrophilic or hydrophobic substance. The present invention is also directed to a nonwoven web comprising a layer having a significant number of nanofibers with diameters less than one micron and a coating substance is applied to a surface of said nanofibers.

## COATED NANOFIBER WEBS

### FIELD OF THE INVENTION

The present invention relates to articles comprising nonwoven webs. More particularly, the invention relates to nanofiber webs containing coated nanofibers.

### BACKGROUND OF THE INVENTION

The need for articles produced from nonwoven containing nanofibers has continued to increase. The nanofibers webs are desired due to their high surface area, low pore size, and other characteristics. The nanofibers, also commonly called microfibers or very fine fibers, typically have diameters of less than 1000 nanometer or one micron. The nanofibers can be produced by a variety of methods and from a variety of materials. Although several methods have been used to make nanofiber nonwoven webs, there are drawbacks to each of the methods and producing cost effective nanofibers has been difficult.

Methods of producing nanofibers include a class of methods described by melt fibrillation. Melt fibrillation is a general class of making fibers defined in that one or more polymers are molten and extruded into many possible configurations, such as co-extrusion, homogeneous or bicomponent films or filaments, and then fibrillated or fiberized into fibers. Nonlimiting examples of melt fibrillation methods include melt blowing, melt film fibrillation, and melt fiber bursting. Methods of producing nanofibers, not from melts, are film fibrillation, electro-spinning, and solution spinning. Other methods of producing nanofibers include spinning a larger diameter bicomponent fiber in an islands-in-the-sea, segmented pie, or other configuration where the fiber is further processed after the fiber has solidified so that nanofibers result.

Melt blowing is a commonly used method of producing fine fibers and webs containing such fibers and additional particulates. The latter is generally referred to as "coforming". Examples of coforming particulates with fine fibers have been given by U.S. Patent Nos. 4,100,324; 4,784,892; and 4,818,464 assigned to Kimberly-Clark Corp. Typical melt-blown fiber diameters range from 1.5 to 10 microns, for example, as utilized in the above methods. Though particulates are mechanically held captive by the microfibers, there is a limitation to the functionality that particulates can provide in fine fiber webs. Therefore, it is desirable to coat the fibers with fluids or very fine particles to attain a desired functionality in the fine fiber webs.

Melt blowing can be used to make fibers with smaller diameters but with considerable changes needed to the process. Commonly, redesigned nozzles and dies are needed. Examples of these include U.S. Patent Nos. 5,679,379 and 6,114,017 by Fabbricante et al. and U.S. Patent Nos.

5,260,003 and 5,114,631 by Nyssen et al and U.S. Patent Application No. 2002/0117782 by Haynes et al. These methods utilize relatively high pressures, temperatures, and velocities to achieve the small fiber diameter. The above-mentioned methods have not been used to make webs with coated nanofibers.

It is an object of the present invention to provide webs containing coated nanofibers. It is also an object of the present invention to provide a method of forming a web from melt film fibrillation comprising coated fibers.

#### SUMMARY OF THE INVENTION

The present invention is directed to a method of forming nonwoven webs comprising coated fibers. The method of forming the nonwoven web generally comprises the steps of forming fibers from a melt fibrillation process, forming at least one fluid stream containing a coating substance, applying the coating substance onto the surface of the fiber, and depositing the coated fibers on a surface to form a web. Typically, the fibers are coated in flight. The same fluid stream may be used to form the fibers and contain the coating or there may be separate fluid streams for forming the fibers and for containing the coating. Preferably, the melt fibrillation process to form the fibers is a melt film fibrillation process. A melt film fibrillation process generally includes the steps of providing a polymeric melt, utilizing a central fluid stream to form an elongated hollow polymeric film tube, and using air to form multiple nanofibers from the hollow tube.

The nonwoven web may comprise a layer having a significant number of nanofibers with diameters less than one micron. The layer may comprise two or more pluralities of fiber diameter distributions wherein at least one plurality has an average fiber diameter of less than about one micron.

The coating substance can be selected from the group consisting of lotions, powders, surfactants, softeners, nanoparticles, creams, gels, conducting fluids, hydrophilic agents, hydrophobic agents, hygroscopic agents, emollients, plasticizers, absorbent gelling material, antimicrobial agents, and combinations thereof. A preferred coating substance is a surfactant. Another preferred coating substance is a hydrophilic or hydrophobic substance.

The present invention is also directed to a nonwoven web comprising a layer having a significant number of nanofibers with diameters less than one micron and a coating substance is applied to the surface of said nanofibers. Preferably, the layer comprises at least about 35% of fibers having a diameter of less than one micron. The nonwoven web can be utilized as an absorbent material, to provide controlled delivery of the coating substance, or for other uses. The coating substances may be selected from the group consisting of catalysts, reactants, or combinations thereof. The article may be selected from the group consisting of dye-eliminating

clothes, odor-eliminating webs, odor-eliminating sheets, odor-eliminating wipes, drug-delivery webs, wound-healing dressings, and combinations thereof.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an illustration of a nozzle and air streams utilized in a melt film fibrillation process.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to articles made from fibers, particularly coated fibers. The fibers are produced from one or more thermoplastic polymers. Nonlimiting examples of thermoplastic polymers suitable for the present invention include polyolefins, polyesters, polyamides, polystyrenes, polyurethanes, biodegradable polymers including starch compositions, PHA, PLA, and combinations thereof. The homopolymer, copolymers, and blends thereof are included within this description. The most preferred polymers are polyolefins such as polypropylene, polyethylene, nylons, and polyethylene terephthalate.

Suitable thermoplastic polymers include any polymer suitable for melt spinning. The rheological properties of the polymer must be such that the polymer can be melt extruded and is able to form a film. The melting temperature of the polymer is generally from about 25°C to 400°C. The polymers of the present invention as they are present in the die may have a melt flow rate of less than about 400 decigrams per minute. The melt flow rate is measured using ASTM method D-1238. Preferably, the melt flow rate may be less than about 300 decigrams per minute, more preferably less than about 200 decigrams per minute, and most preferably less than about 100 decigrams per minute. A most preferred range for melt flow rates is from about 1 decigram per minute to about 100 decigrams per minute. Generally, the lower the melt flow rate the more preferred. Therefore, polymers with melt flow rates less than about 50 decigrams per minute and 30 decigrams per minute can also be used.

The fibers may be single or multicomponent fibers such as bicomponent fibers. The fibers may have a sheath-core or side-by-side or other suitable geometric configuration. After the fibers are made, the fibers may be treated or coated before formed into a web. Additionally, after a web is made, the web may be treated. Optionally, additives may be compounded into the polymer resin and these additives may move out to the surface of the fiber after the fibers are formed. The additives that migrate to the surface may need to be cured utilizing external energy, such as heat, or additives on surface may need to be chemically reacted with another component or curing may need to be catalyzed in the presence of another component, such that additional components may be added to the process while the fibers are being made or after the fibers are

made using the resin with additives. Suitable treatments include hydrophilic or hydrophobic treatments. An example of hydrophobic treatment is poly-di-methyl-siloxanes. The specific treatment depends on the use of the web, type of polymer, and other factors.

Optionally, the polymer may contain additional materials to provide other properties for the fiber. These optional materials are typically added to the polymer melt and are not the coating substance which is applied to the melt fibrillation formed fibers. The optional materials may modify the physical properties of the resulting fiber such as elasticity, strength, thermal and/or chemical stability, appearance, absorbency, odor absorbency, surface properties, and printability, among others. A suitable hydrophilic melt additive may be added. Optional materials may be present up to 50% of the total polymer composition.

The coating substance is applied to the fibers, preferably formed by the melt fibrillation process. The coating substance can be any substance that is able to be coated on a fiber. The coating substance may be a solid or a fluid. Solids that are hard to coat can be mixed with liquids and then coated on the surface of the fibers. The coating substance may be selected from the group consisting of lotions, creams, gels, emollients, fluids, powders, nanoparticles, and combinations thereof. Other suitable coating substances include surfactants, softeners, conducting fluids, hyphilic agents, hydrophobic agents, hygroscopic agents, plasticizers, absorbent gelling materials, antimicrobial agents, and combinations thereof. Other suitable coating substances are sodium bicarbonate, activated carbon, calcium carbonate, cyclodextrin, titanium dioxide, minerals, pigments, powdered detergents, waxes, super absorbent polymers or combinations thereof. Nonlimiting examples of super absorbents polymer include those formed from hydrolyzed cross-linked polyacrylamides, polyacrylates, polymers of acrylic polymers, or their copolymers. Suitable odor-controlling substances suiting for coating include activated charcoal or active carbon, baking soda, chitin, deodorizing materials such as clays, diatomaceous earth, zeolites, and complexes of potassium permanganate with active alumina, and combinations thereof.

The method of making the nanofibers of the present invention is any melt fibrillation process that is suitable for applying a coating substance onto the fibers. Melt fibrillation processes are defined as a process utilizing a single phase polymer melt wherein fibers are formed. Single phases can include a dispersion but do not include solvent based melts such as those used in solution or electrospinning. Typical single step melt fibrillation processes include melt blowing, melt film fibrillation, spun bonding, melt spinning in a typical spin/draw process, and combinations thereof. The process may include a two step process where the fiber is first made and then split or a part is dissolved to make smaller diameter fibers (e.g. segmented pie or islands-in-the-sea) after the fiber has solidified.

Preferably, a melt film fibrillation process is used. Generally, this process involves providing a polymeric melt, utilizing a central fluid stream to form an elongated hollow polymeric film tube, and then using air to form multiple nanofibers from the hollow tube. Suitable methods are described in, for example, U.S. Patent No. 4,536,361 to Torobin and U.S. Patent Nos. 6,382,526 and 5,520,425 to Reneker. The melt film fibrillation methods can utilize different processing conditions. Reneker's method more specifically includes the steps of feeding the polymer into an annular column and forming a film or tube at the exit of the annular column where a gas jet space is formed. A gas column then provides pressures on the inner circumference of the polymer tube. When the polymer tube exits the gas jet space, it is blown apart into many small fibers, including nanofibers, due to the expanding central gas.

An example of a melt film fibrillation method is further illustrated in Figure 1. This preferred embodiment illustrates a nozzle 7 with orifice 7a which forms the nanofibers 17. The process more specifically includes the steps of melting the polymer composition 2 and forming a liquid film 9 across an orifice 7a. The polymer composition will contain the polymer and any other desired ingredients. The polymer composition 2 is extruded through an orifice 7a which in turn contains a central fluid stream 10 such that the polymer 2 extrudes as an elongated hollow tube 12. The orifice 7a may be part of a nozzle 7 and the nozzle 7 may be optimized for process stability. A fiberizing fluid 10, such as a central fluid stream, is blown to form an elongated hollow tube 12. The fiberizing fluid 10 will then provide pressure on the inner surface of the elongated hollow tube 12. Thinned wall or weakened portions may form in the hollow tube 12 to more easily and controllably enable the formation of fibers including nanofibers 17. The weakened portions may result from notches or projections located on the outer surface of the central fluid jet 10 or on the inner surface of the polymer extrusion orifice 7a. The elongated hollow polymeric film tube 12 is then subjected to a fluid to form the fibers 17. This fluid can be the central fluid stream 10 or an entraining fluid 14 or any fluid stream. The fluid stream may induce a pulsating or fluctuating pressure field which forms a multiplicity of fibers including nanofibers 17. The entraining fluid 14 is from transverse jet 13. If advantageous, a nozzle 18 providing cooling or heating fluid 19 to the formed nanofibers 17 may be used.

The polymer 2 is typically heated until it forms a liquid and flows easily. The melted polymer 2 may be at a temperature of from about 0°C to about 400°C, preferably from about 10°C to about 300°C, and more preferably from about 20°C to about 220°C. The temperature of the polymer 2 depends on the melting point of the polymer or polymer composition. The temperature of the polymer 2 is less than about 50°C above its melting point, preferably less than 25°C above its melting point, more preferably less than 15°C above its melting point, and just at

or above its melting point or its melting range. The melting point or range is measured by ISO 3146 method. The melted polymer 2 will typically have a viscosity of from about 1 Pa·s to about 1000 Pa·s, typically from about 2 Pa·s to about 200 Pa·s and more commonly from about 4 Pa·s to about 100 Pa·s. These viscosities are given over a shear rate ranging from about 100 to about 100,000 per second. The melted polymer 2 is at a pressure of about atmospheric pressure or slightly elevated.

The elongated hollow polymer tube can be circular, elliptical, irregular, or any other shape which has a hollow region. In some cases, the elongated hollow polymer tube may collapse immediately after forming. In the case of the collapsed tube, it may be preferred to have thinned walls or weakened portions in the tube to aid in the fibrillation. Non-limiting examples of the fiberizing fluid are gases such as nitrogen or more preferably air. The fiberizing fluid 10 can be at a temperature close to the temperature of the melted polymer 2. The fiberizing fluid 10 temperature may be at a higher temperature than the melted polymer 2 to help in the flow of the polymer 2 and the formation of the hollow tube 9. Alternatively, the fiberizing fluid 10 temperature can be below the melted polymer 2 temperature to assist in the formation and solidification of the nanofibers 17. Preferably, the fiberizing fluid temperature is less than the polymer melting point, more preferably more than 50°C below the polymer melting point, more preferably more than 100°C below the polymer melting point, or just at ambient temperature. The pressure of the fiberizing fluid 10 is sufficient to fibrillate the nanofibers 17 and can be slightly above the pressure of the melted polymer as it is extruded out of the orifice 7a.

The fiberizing fluid 10 may have a velocity of less than about 500 meter per second. Preferably, the fiberizing fluid velocity will be less than about 100 meter per second, more preferably less than about 60 meter per second, and most preferably from about 10 to about 50 meters per second. The fiberizing fluid may pulsate or may be a steady flow. Although it is critical that this fiberizing fluid is present to aid in the formation of the elongated hollow polymeric film tube, the amount of fluid in this stream may be very low.

The polymer 2 throughput will primarily depend upon the specific polymer used, the nozzle design, and the temperature and pressure of the polymer. The polymer 2 throughput will be more than about 1 gram per minute per orifice. Preferably, the polymer throughput will be more than about 10 gram per minute per orifice and more preferably greater than about 20 gram per minute per orifice, and most preferably greater than about 30 gram per minute per orifice. There will likely be several orifices 7a operating at one time which further increases the total production throughput. The throughput, along with pressure, temperature, and velocity, are measured at the die orifice exit 7a.

The fibrillation and solidification of the fibers may occur before the fibers and fluid exit the orifice. Once the elongated hollow tube exits the orifice, the nanofibers are formed. Commonly, the formation of nanofibers occurs immediately upon exiting the orifice. One or more fluid streams are used to form the multiplicity of nanofibers. The fluid stream can be the central fluid stream, an entraining fluid, or any other fluid stream. An entraining fluid 14 can be used to induce a pulsating or fluctuating pressure field to help in forming a multiplicity of nanofibers 17. As shown in Figure 1, the entraining fluid 14 may be provided by a transverse jet 13 which is located to direct the flow of entraining fluid 14 over and around the hollow elongated tube 12 and nanofiber 17 forming region. The entraining fluid 14 can have a low velocity or a high velocity, such as an near sonic or super sonic speeds. An entraining fluid with a low velocity will typically have a velocity of from about 1 to about 100 meter per second and preferably from about 3 to about 50 meter per second. The temperature of the entraining fluid 14 can be the same as the above fiberizing fluid 10, ambient temperature, or a higher temperature, or a temperature below ambient.

An additional fluid stream, a quench or heating fluid 19, can also be used. This additional fluid stream 19 is located to direct fluid into the nanofibers 17 to cool or heat the fibers. If the additional fluid is used as a quenching fluid, it is at a temperature of from about -20°C to about 100°C and preferably from about 10°C to 40°C. If the additional fluid is used as a heating fluid, it is at a temperature of from about 40°C to 400°C and typically from about 100°C to about 250°C. Any fluid stream may contribute to the fiberization of the polymer melt and can thus generally be called fiberizing fluids.

Any of the fluid streams, including the central fluid stream, an entraining fluid, or additional fluid stream, may contain a treatment, additive, coating, or other substance or particulate for changing the surface, chemical, physical, or mechanical properties of the fibers produced.

The coating substance may be present in one or more of the above described fluid streams. The fluid streams are described as the fiberizing fluid 10 that forms the hollow tube, the entraining fluid 14, and/or the cooling or heating fluid 19. Each of these fluid streams can be considered a fiberizing fluid stream as they may all contribute to the formation of the fiber, but the streams are referred to for clarity as the fiberizing fluid stream 10, entraining fluid stream 14, and heating/cooling fluid stream 19. The coating substance may be included in any of the fluid streams or any combination of the streams. Typically, the coating substance will be included in the fiberizing fluid stream 10. Determination on which fluid stream the coating substance will be added to depends upon the coating substance, such as whether the substance is heat stable and the

viscosity or form (e.g., gel, liquid, powder, etc.) of the substance; how the coating substance should be combined with the fibers (coat all of the fibers or just some of the fibers, how thick the coating should be); how much of the coating substance is being added; and other factors relevant in producing the web containing the coated fibers. The heating/cooling fluid stream 19, when utilized as a quench stream, can evaporate the liquid from the coating substance and leave solid on the surface of the fiber. The coating substance may cover all of the fibers or just part of the fibers. The substance may cover only one side of the fiber or the entire fiber surface. This can be controlled by the selection of the fluid stream used, the temperatures, the composition and size of the fibers, and the particular coating substance used, among other things.

Once the fluid stream containing the coating substance contacts the surface of the fiber, a coated fiber is formed. Preferably, the coated fibers remain in flight until they are deposited onto a surface and a web is formed.

The fibers are laid down on a collector to form a web. The collector is typically a conveyor belt or a drum. The collector is preferably porous and vacuum may be applied to provide suction to aid fiber lay down on the collector. The distance from the orifice to the collector distance, commonly called die-to-collector distance (DCD), can be optimized for desired web properties. It may be desired to utilize more than one DCD used in a web, to change the DCD during production, or to have different beams with different DCDs. It may be desirable to form a web with different uniformities by changing the DCD.

After the elongated hollow film tube is formed, the tube or the fibers may alternatively be subject to an additional process that further promotes the formation of nanofibers. The further processing would occur immediately after formation of the elongated hollow polymeric film tube and before the fibers have solidified to still be considered a single step process. The additional processing can utilize one or more Laval nozzles to speed up the gas velocities to sonic and/or supersonic range. When polymer melt is exposed to such high gas velocities, it bursts into multiplicity of fine fibers. Examples of a Laval nozzle are described in Nyssen et al., US Patent No. 5,075,161, in which a method of bursting polyphenylene sulfide melt into fine filaments is disclosed. The Laval nozzle may be positioned just after the spinning nozzle when the elongated hollow polymeric film tube is produced. Alternatively, Laval nozzle could be positioned just after the fibers have formed to further reduce the fiber size. Polymer fibers can be produced by subjecting the polymer melt streams to drawing out and cooling to below the melt temperature by extruding them into a gaseous medium which flows essentially parallel to the polymer melt streams and attains sonic or supersonic speed. This simultaneous deformation and cooling gives rise to amorphous fine or extremely fine fibers of finite length. High speed fiber bursting

minimizes the surface oxidation of the fibers. The spinning speed, melt temperature, and the position of the Laval nozzle are appropriately set to achieve only partial thermal oxidation of fine filaments at their surface.

Various processes and combination of processes can be used to make the webs of the present invention. Melt fiber bursting, as disclosed in WO 04/020722 by Sodemann et al., can be combined with melt film fibrillation of the present invention on two separate beams on a single line. Various aspects of melt fiber bursting can be incorporated into melt film fibrillation, such as producing fibers of different strengths and diameters to provide a desired combination of properties. Alternatively, aspects of melt film fibrillation can be included in other melt fibrillation processes to increase the throughput rate by utilizing a hollow elongated tube to form fibers. For example, the melt film fibrillation process of the present invention could be modified to include a Laval nozzle to aid in drawing down the fibers. Drawing down can aid in further attenuation and increase the strength of the fibers. This may be particularly preferred for high Tg polymers such as polyesters in which stress-induced crystallization happens at speeds in excess of 4000 m/min.

The coated fibers of the present invention are used to make nonwoven webs. The web is defined as the total nonwoven composite. A web may have one or several layers. A layer is the web or part of a web that is produced in a separate fiber lay down or forming step.

The webs of the present invention may comprise one or more layers having a significant number of nanofibers having diameters of less than one micron. A significant number is defined as at least about 25%. The significant number of fibers can be at least about 35%, at least about 50%, or more than 75% of the total number of fibers in the layer. The web could have 100% of the fibers having a diameter of less than about one micron. The fiber diameters of the web can be measured using a scanning electron microscope at a magnification of greater than about 500 times and up to about 10,000 times as needed for visual analysis. To determine if a significant number of fibers have diameters less than one micron, at least about 100 fibers and preferably more fibers should be measured. The measurements should occur at various regions throughout the layer and sufficient sampling that is statistically significant is preferred.

If a significant number of the fibers have a diameter of less than about one micron, the fiber diameter of the remaining larger fibers may have fiber diameters in any range. Typically, the larger fiber diameters will be just above one micron to about 10 microns.

Preferably, a significant number of fibers in a layer will have a fiber diameter of less than about 900 nanometer and more preferably from about 100 nanometers to about 900 nanofibers. The fibers may have a diameter of less than 700 nanometers and from about 300 to about 900 nanometers. The preferred diameters depend upon the desired use of the web. For process and product benefits, it may be desirable in some applications to have a significant number of fibers

having a diameter of less than about one micron and a significant number of fibers having a diameter of greater than about one micron. The larger fibers may trap and immobilize the nanofibers. This may help to reduce the amount of clumping or roping of the nanofibers and prevents the nanofibers from being carried off by stray air currents.

The layers of fibers in a web of the present invention may contain more than one polymer. Different polymers or polymer blends may be used for different orifices to produce layers in a web having different fiber diameters and different polymer compositions. One or more layers of the web may contain the coated fibers.

It may be desirable to produce a single layer nonwoven with varying fiber diameters. Alternatively, it can be desired to produce a nonwoven web with multiple layers with each layer having different fiber diameters. The melt film fibrillation process can be modified to produce both small and large diameter fibers to make various webs. The smaller fiber diameters are referred to as having a significant number of fibers having a diameter of less than one micron. The larger diameter fibers include fibers from the melt blowing range (typically 3 to 5 microns) to the spunbond (typically around 15 microns) or any range of fiber diameters above 1 micron. For example, one layer can be produced with an average fiber diameter of less than one micron and another layer with an average fiber diameter of around 5 microns. This type of structure could be used where traditionally SMS webs are used. Another example is to produce a nanofiber web with multiple layers, with each layer having a distinct average fiber diameter such as one layer having an average fiber diameter of 0.4 micron and a second layer having an average fiber diameter of 0.8 micron. The webs with various fiber diameters can be produced on the same line with the same equipment. This is an inexpensive way as the same equipment and components can be used. The operating costs and equipment costs are both controlled. Also, if desired, the same polymer can be used to produce different fiber diameters.

It may be desired to form a web of several layers. The nanofiber layer may be combined with one, two or more layers. A spunbond-nanofiber-spunbond web is one example. Basis weights for the total composite webs range from about 5 gsm to about 100, preferably from about 10 to about 100 gsm, and more preferably from about 10 gsm to about 50 gsm. For use as a barrier layers, the total composite web basis weight may be from about 10 gsm to about 30 gsm. The basis weight of only the nanofiber layer is from about 0.5 gsm to about 30 gsm and preferably from about 1 gsm to about 15 gsm.

After the nonwoven is made, it may be subject to post processing. Nonlimiting examples of post processing include solid state formation, consolidation, lamination, surface coating, corona and plasma treatment, dyeing, and printing. Nonlimiting examples of solid state formation include processes using intermeshing rolls, such as in U.S. Pat. No. 5,518,801 and referred to in

subsequent patent literature as "SELF" webs, which stands for "Structural Elastic-like Film", texturing, stretching, aperturing, laminating, local straining, micro creping, hydroforming, and vacuum forming. Nonlimiting examples of consolidation include thermal bonding, through air bonding, adhesive bonding, and hydroentangling.

The articles of the present invention will contain the above described nonwoven webs. The web may comprise the entire articles, such as a wipe, or the web may comprise one component of the article, such as a diaper. Preferred articles include hygiene articles such as diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and personal care wipes including baby wipes, facial wipes, body wipes, and feminine wipes. Personal care articles include articles such as wound dressings, active delivery wraps or patches, and other substrates that are applied to the body, particularly the skin. Other articles includes filters for fluids such as air and water, industrial wipes for automobiles, clean rooms, surface cleaning, food, and other uses, absorbent materials for fluids such as oil, water, alcohol, organic and inorganic liquids.

In a diaper, the web may be used as a barrier layer or an outercover with odor or liquid absorbent coating substances. The webs may also be used as a high barrier cuff to enable low leakage incident rates of thin, narrow crotch diapers desired for comfort and fit. The webs containing absorbent coating substances may be used in wipes to enable improved lotion handling and reduced gradient of liquids. The webs may also provide controlled delivery. This delivery can be of liquids, lotions, actives, perfumes, or other materials. Alternatively, the fibers of the webs may be coated with lotions, liquids, actives, perfumes, or other suitable coating substances. Due to the high surface area of the nanofibers, and preferably coating substances which are liquid absorbent, the webs may be used as absorbent materials for wipes or cores of feminine care product pads, diapers, training pants, or adult incontinence. The webs may provide further enhanced distribution of fluids and retention and certain layers of the webs may have different properties. The nonwoven webs could also be coated with substances that may change the opacity or color of the web as desired in the articles. Preferred coating substances for the desired opacity or color may include pigments, titanium dioxide, inorganic or organic crystals.

Where there is a large surface area from nanofibers, the nanofiber web can act as a reactant or catalyst carrying substrate for applications where *in-situ* chemical reactions or adsorption of reactants is required. Catalyst or reactants can be a part of coating substance. Nonlimiting examples of products where reactants or catalysts are coated on nanofiber web of present invention include dye-eliminating cloths during wash cycle of laundry where dye neutralizing reactants are coated on nanofibers; odor eliminating wipes for clothes (can be included in the dryer) such that odor neutralizing reactants are coated on fibers and in presence of

heat react with odors and neutralize odors; odor eliminating web included in core of diapers, catamenials products, feminine hygiene pads, adult incontinence products where one of the reactants is bio-fluid and other reactant is coated on nanofibers to neutralize odors; odor eliminating sheets for refrigerators, automobiles, or places where such products may be required; drug delivery bio-polymer webs where drug to be delivered is coated on nanofibers; wound-healing dressing where antimicrobial reactants are coated on nanofibers. Other products that will benefit from a web of the present invention include a personal filter or mask such as a surgical mask. Other medical uses of the webs include surgical gowns, wound dressings, and medical barriers.

In a diaper or other disposable absorbent product, the nonwoven web of the present invention may be utilized as a barrier layer. The barrier layer may be disposed between an absorbent core and an outer layer of the disposable absorbent product. The absorbent core is the component of the article that is primarily responsible for fluid handling properties such as acquiring, transporting, distributing, and storing body fluids. The absorbent core is typically located between a liquid pervious body-side inner layer and a vapor permeable, liquid impermeable outer cover. The outer layer, also known as the back sheet or outer covering, is located on the outside of the disposable product. In the case of a diaper, the outer layer contact the user's garment or clothing. The barrier layer may alternatively or also be disposed between the absorbent core and an inner layer. The inner layer, also known as a top sheet, is located on the side closest to the user's skin. The inner layer may contact the user's skin or may contact a separate top sheet with contacts the user's skin. The barrier layer may be absorbent. The nonwoven web may comprise the layer around the absorbent core and help to distribute or handle fluids. The nonwoven web may be a fluid distribution layer, which may be located adjacent to the core. The barrier layer most preferably has a balance between convective air flow and absorptive barrier property. The convective air flow property is effective to reduce the relative humidity within the space between the absorbent article and the wearer's skin. The combination of liquid absorption and liquid barrier property provides protection against the wet through problem and is especially beneficial when the absorbent article is under impact and/or sustained pressure. Further description and benefits of the barrier layers may be found in WO 01/97731.

The webs may be used to make hygiene wipes that are dry or pre-moistened. The webs may be used in wipes to enable improved lotion handling and reduced gradient of liquids. The web of the present invention may provide a partial barrier and may be partially or completely liquid impervious. The webs may also provide controlled delivery of a substance or active such as a drug. The delivered substance can be liquids, lotions, enzymes, catalysts, actives, or other materials such as emollients, surfactants, wetting agents, polishes, oils, organic and inorganic

solvents, pastes, gels, pigments, or dyes. The webs may provide enhanced distribution of fluids and/or retention. Additionally, the webs for absorbent uses may be made with added particulates or absorbent or natural fibers for increased absorbance or certain layers of the webs may have different properties. The fibers may be produced to be low density or porous fibers. The fibers may be produced with an inlatent or blowing agent.

Due to the high surface area of nanofibers, the webs containing coated nanofibers may be used as absorbent materials for wipes or cores of feminine care product pads, diapers, training pants, or adult incontinence. The high surface area also enhances cleaning and may be used in hygiene cleaning wipes. The webs may provide enhanced distribution of fluids and/or retention. Additionally, the webs for absorbent uses may be made with added particulates or absorbent or natural fibers for increased absorbance or certain layers of the webs may have different properties.

The coated fiber webs may also be used in articles wherein opaqueness is desired. Added opaqueness may result due to the small fiber diameter and uniformity; or pigments may be added to the polymer melt or webs. The webs may also be low linting resulting from longer length fibers or entangling of fibers in the web. The tensile strength of nanofiber webs of the present invention can be greater than the tensile strength of webs with similar fiber diameters and similar basis weights made from other processes. The webs of the present invention will be soft and may be softer than other webs with the same performance.

The fiber diameter can be measured using a Scanning Electronic Microscope (SEM) and image analysis software. A magnification of 500 to 10,000 is chosen such that the fibers are suitably enlarged for measurements. Image analysis software for automatic sampling of fiber diameter in the SEM picture is possible, but also a more manual procedure can be used. In general, the edge of a randomly selected fiber is sought and then measured across the width (perpendicular to fiber direction at that spot) to the opposite edge of the fiber. A scaled and calibrated image analysis tool provides the scaling to get the actual reading in mm or micrometers ( $\mu\text{m}$ ). Several fibers are randomly selected across the sample of web in the SEM. Typically, several samples from a web are cut and tested in this manner and at least about 100 measurements are made and all data are recorded for statistic analysis. If the result is to be recorded in denier, then the following calculation needs to be made. Diameter in denier = Cross-sectional area \* density \* 9000m \* 1000 g/kg. The cross-sectional area is  $\pi \times \text{diameter}^2/4$ . The density for PP, e.g., can be taken as 910 kg/m<sup>3</sup>. To obtain decitex (dtex), the 9000m is replaced by 10,000m.

Basis weight can be measured consistent with compendial methods ASTM D 756, ISO 536 and EDANA ERT-40.3-90. Basis weight is defined as mass per unit area, with grams per square meter (gsm) as the preferred unit. Required instruments are a scissors or a die-cutter for

sample cutting and an accurate weighing device, such as a scale. A sample is cut to a total area of 100cm<sup>2</sup> per layer with an accuracy and precision of  $\pm 0.5\%$ . A scale or balance is needed with 0.001 g sensitivity, readable, calibrated and accurate to within 0.25% of the applied load. The samples are conditioned at 23° Celsius ( $\pm 2^\circ\text{C}$ ) and at a relative humidity of about 50% for 2 hours to reach equilibrium. Weigh the cut sample with 10 plies from the sample area for a total of 1000cm<sup>2</sup> = 0.1 m<sup>2</sup> on an analytical balance to the nearest 0.001g and record the weight. (For samples thicker than 1mm, weighing only 1 ply is preferred but should be noted.) Calculate the basis weight by dividing the weight by the sample area (all layers tested) to give the basis weight in gsm. All data are recorded for statistic analysis.

Web uniformity can be measured through several methods. Examples of uniformity metrics include low coefficient of variation of pore diameter, basis weight, air permeability, and/or opacity. Uniformity also requires lack of fiber bundles or roping, or visible holes, or other such defects. Uniformity can be controlled by process modification such as reducing the nozzle to collector distance. The reduction in this distance reduces the fiber bundling or roping and can provide more uniform webs.

Pore diameter can be determined by methods known to those skilled in the art. The mean pore diameter is preferably less than about 15 microns, more preferably less than about 10 microns, and most preferably less than about 5 microns. The desired coefficient of variation for a uniform web is less than 20%, preferably less than about 15%, and more preferably about 10% or less. The lack of roping can be measured by counting the number of ropes or bundles of fibers in a measured area of the web. The lack of holes is also measured the number of holes having a diameter above a certain threshold in a measured area of the web. The holes may be counted if they are visible to the naked eye or are more than 100 microns in diameter.

All documents cited are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## WHAT IS CLAIMED IS:

1. A method of forming a nonwoven web comprising the steps of:
  - a. forming fibers from a melt film fibrillation process,
  - b. forming at least one fluid stream containing a coating substance,
  - c. applying the coating substance onto the surface of the fiber, and
  - d. depositing the coated fibers on a surface to form a web.
2. The method according to Claim 1 wherein the fibers have a diameter of less than 1 micron.
3. The method according to Claim 1 wherein the fibers are formed in the melt film fibrillation process in a first fluid stream and the coating substance is applied in a second fluid stream.
4. The method according to Claim 1 wherein the fibers are formed in the melt film fibrillation process in a first fluid stream and the coating substance is applied from the same first fluid stream.
5. An article comprising a nonwoven web produced according to Claim 1.
6. The article according to Claim 5 wherein the article is selected from the group consisting of diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and wipes such as baby wipes, facial wipes, feminine wipes, surface cleaning wipes, automobiles, clean rooms, surface cleaning, food, and other uses, filters for fluids such as air and water, absorbent materials for fluids such as oil, water, alcohol, organic and inorganic liquids, and combinations thereof.
7. A nonwoven web comprising a layer having a significant number of nanofibers with diameters less than one micron, wherein a coating substance is applied to a surface of said nanofibers.

8. The nonwoven web according to Claim 7 wherein the layer comprises two or more pluralities of fiber diameter distributions wherein at least one plurality has a fiber diameter of less than about one micron.
9. An article comprising the nonwoven web according to Claim 7.
10. The nonwoven web according to Claim 7 wherein the layer comprises at least 35% of nanofibers having a diameter of less than one micron.

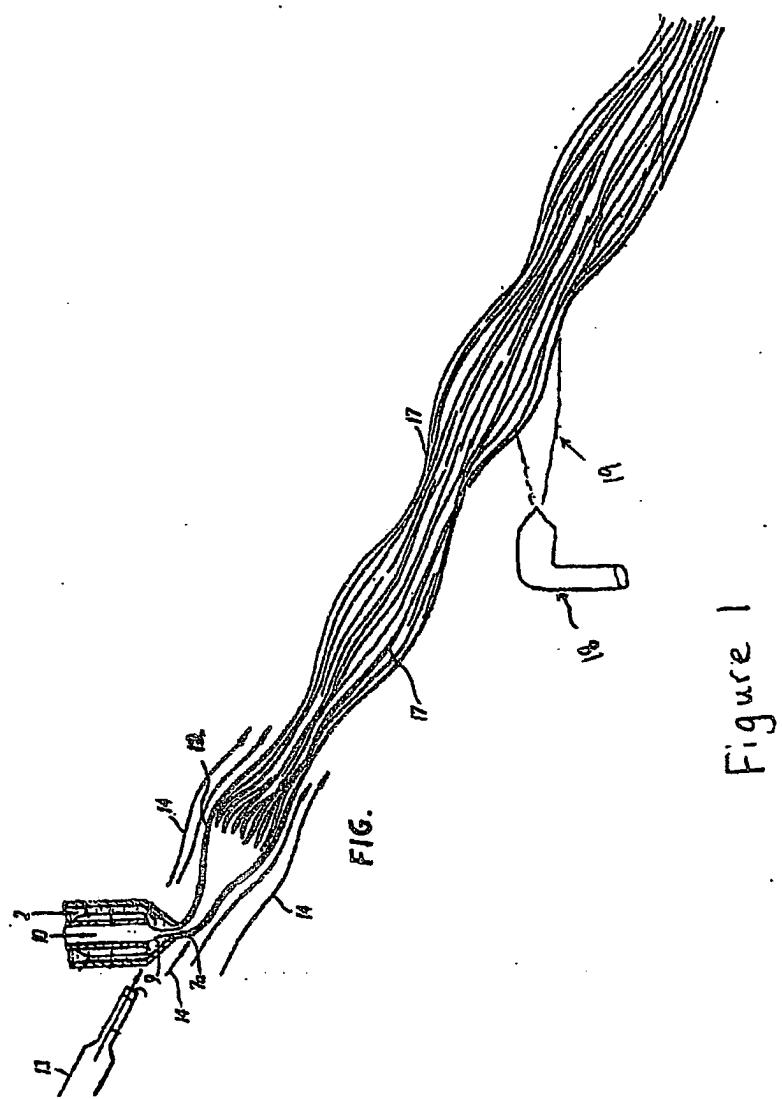


Figure 1

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/021126A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 D01D5/42 D04H1/42 A61F13/15 D06M23/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 D01D D04H A61F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 4 536 361 A (TOROBIN LEONARD B) 20 August 1985 (1985-08-20) cited in the application column 2, line 54 - column 3, line 2; figures 1-4	1-6
Y	US 6 382 526 B1 (RENEKER DARRELL H ET AL) 7 May 2002 (2002-05-07) cited in the application column 2, line 16 - column 3, line 10; figures 1-7	1-6
Y	DE 199 23 344 A (COROVIN GMBH) 23 November 2000 (2000-11-23) page 3, line 16 - line 19; claims 1-22; figure 1	1-6

 Further documents are listed in the continuation of box C Patent family members are listed in annex

## \* Special categories of cited documents

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

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25 November 2004

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## INTERNATIONAL SEARCH REPORT

International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 6 395 046 B1 (RAABE ERNST ET AL) 28 May 2002 (2002-05-28) column 2, line 19 – column 3, line 27; claims 1-25 column 5, line 18 – line 19 -----	7-10
A	WO 03/043809 A (POLYMER GROUP INC) 30 May 2003 (2003-05-30) page 3, line 11 – page 4, line 25; claims 1-24 -----	7-10

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US2004/021126

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4536361	A	20-08-1985		AU 1044683 A	17-06-1983
				CA 1200355 A1	11-02-1986
				EP 0095487 A1	07-12-1983
				GB 2112704 A	27-07-1983
				WO 8301925 A1	09-06-1983
				CA 1149170 A1	05-07-1983
				CA 1150017 A1	19-07-1983
				CA 1126033 A1	22-06-1982
				CA 1150055 A2	19-07-1983
				CA 1171284 A2	24-07-1984
				CA 1169211 A2	19-06-1984
				DE 2950447 C2	01-08-1991
				DE 2950447 T0	15-01-1981
				DE 2954563 C2	20-09-1990
				EP 0016818 A1	15-10-1980
				EP 0015293 A1	17-09-1980
				EP 0018410 A1	12-11-1980
				EP 0080078 A2	01-06-1983
				EP 0226738 A1	01-07-1987
				GB 2048847 A ,B	17-12-1980
				GB 2042963 A ,B	01-10-1980
				GB 2050345 A ,B	07-01-1981
				GB 2082190 A ,B	03-03-1982
				GB 2083099 A ,B	17-03-1982
				GB 2081877 A ,B	24-02-1982
				GB 2112769 A ,B	27-07-1983
				GB 2113668 A ,B	10-08-1983
				GB 2112923 A ,B	27-07-1983
				GB 2111971 A ,B	13-07-1983
				JP 1598026 C	28-01-1991
				JP 2005695 B	05-02-1990
				JP 61275137 A	05-12-1986
				JP 1038531 B	15-08-1989
				JP 1574406 C	20-08-1990
				JP 57140642 A	31-08-1982
				JP 1408581 C	27-10-1987
				JP 57140323 A	30-08-1982
				JP 62010931 B	09-03-1987
				JP 1009547 B	17-02-1989
				JP 1524937 C	12-10-1989
				JP 57142450 A	03-09-1982
				JP 1758451 C	20-05-1993
				JP 3115130 A	16-05-1991
				JP 4046910 B	31-07-1992
				JP 1630051 C	20-12-1991
				JP 2034897 B	07-08-1990
				JP 61097145 A	15-05-1986
				JP 1657967 C	21-04-1992
				JP 2258650 A	19-10-1990
				JP 3024413 B	03-04-1991
US 6382526	B1	07-05-2002	AU	2705600 A	01-05-2000
			WO	0022207 A2	20-04-2000
DE 19923344	A	23-11-2000	DE	19923344 A1	23-11-2000
			AU	5962300 A	12-12-2000
			WO	0071797 A1	30-11-2000
			DE	10081377 D2	29-05-2002

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/021126

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
DE 19923344	A		EP 1187949 A1	20-03-2002
US 6395046	B1	28-05-2002	DE 19919809 A1 CA 2305004 A1 EP 1048335 A1	09-11-2000 30-10-2000 02-11-2000
WO 03043809	A	30-05-2003	EP 1448365 A1 WO 03043809 A1 US 2003129909 A1	25-08-2004 30-05-2003 10-07-2003